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LA-UR--89-2864

DE89 016983

TITLE SHOCK INDUCED DISSOCIATION OF POLYETHYLENE

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SUBMITTED TO 1989 APS TOPICAL CONFERENCE ON SHOCK COMPRESSION
OF CONDENSED MATTER
14-17 AUGUST 1989
ALBUQUERQUE, NM

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SHOCK INDUCED DISSOCIATION OF POLYETHYLENE*

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To identify the physical processes occurring on the Hugoniot, shock-recovery experiments were performed. Cylindrical recovery systems were used that enabled a wide range of single-shock Hugoniot states to be examined. Mass spectroscopy was used to examine the gaseous dissociation products. X-ray and TEM measurements were made to characterize the post-shock carbon structures. A dissociation product equation of state is presented to interpret the observed results. Polyethylene (PE) samples that were multiply shocked to their final states dissociated at much higher pressures than single-shocked samples.

1. INTRODUCTION

Polyethylene (PE) $(-CH_2-CH_2-)_n$ is used in a variety of applications where a material of low shock impedance with excellent insulating properties is required. Carter and Marsh¹ (CM) observed a high-pressure phase transition on the Hugoniot, which they postulated to be a solid-solid phase transition into a tetragonally bonded carbon structure. Alternatively, Lee² suggested this transformation was a dissociation reaction to carbon in the diamond phase and hydrogen in a condensed molecular phase. To investigate the nature of this phase transformation, shock-recovery experiments were performed on both single- and multiple shocked PE samples.

2. EXPERIMENT

To identify the phenomenology occurring along the Hugoniot, it is crucial to duplicate these single-shock states. A recovery assembly that produces single-shock states is shown in Fig. 1. A 1.5 mm diam, 51 mm long high density (0.954 gm/cm^3) PE sample is laced in a 6.35 mm diam brass tube. This tube is laced into a second stainless steel (SS) tube that is 2.7 mm diam. SS end plugs are welded into place to provide axial confinement and to hermetically seal the capsule. To prevent excessive heating of the PE during welding the capsule was cooled to keep the PE near ambient conditions. This capsule was then glued to plywood base along with another thick walled steel (2.5 mm inside diam, 51 mm outside diam). The outer steel tube provides a reservoir for nitromethane

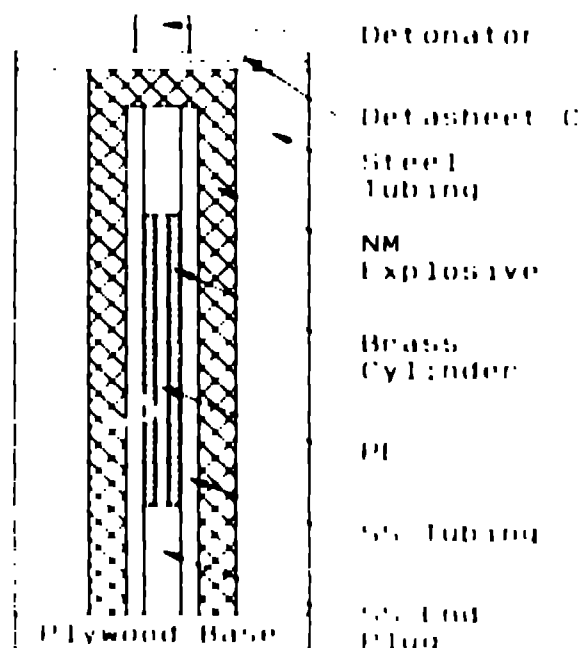


FIGURE 1

Cylindrical recovery system. A sweeping detonation wave in nitromethane (NM) produces a steady state Mach compression wave in the polyethylene (PE) sample.

NM) and also inertial confinement, so that a minimum of explosive is required. To detonate the NM two 1.5 mm thick sheets of Detasheet C are placed on top of the cylinder and detonated with an EBW detonator that was centered on the cylinder. For Detasheet D and Comp C, these explosives were also placed symmetrically around the recovery capsule and detonated on axis. For these explosives, mercury was used to fill the space between the outer confinement tube and the capsule. In this manner, suitable confinement was

*The work was supported by the US Department of Energy.

vided without having to machine parts to close tolerances. NM, Detasheet D, and Comp C were used because these explosives did not have to be machined. This is allowed us to make inexpensive recovery systems. The detonation velocities also spanned a sufficient velocity range so that PE could be shocked to states both above and below the transition pressure.

As the detonation wave travels down the cylinder, eventually a steady state Mach compression wave is formed. The evolution to steady state and the diameter of the Mach disk relative to high explosive (HE) has been examined for some cylindrical geometries.³ The steady state phase velocity of this Mach compression wave is equal to the detonation velocity of the explosive and is independent of the contents of the compressed capsule. If the EOS of the sample is known, the peak pressure in the Mach disk for one-dimensional (1D) flow can be calculated from the detonation velocity of the explosive, because this is the shock velocity of the Mach disk that results in the compression of the sample. In our experiments the diameter of the Mach disk was made equal to or greater than the diameter of the sample cavity by suitable choice of explosive thickness and outer confinement. For this geometry there is not a simple relationship between Mach disk velocity and sample pressure because the Mach disk compression is longer 1D. The Mach disk pressure was varied by using explosives with different detonation velocities. In our experiments, NM, Detasheet D, and Comp C were used. Their detonation velocities are respectively 2 km/s, 7.2 km/s, and 8.0 km/s. The Mach disk pressure in these particular experiments will be discussed later.

One problem encountered in recovering hermetically sealed capsules was that, when the compression wave reached the end plug, a reflected shock was transmitted back into the sample due to the mismatch in shock impedances between SS and PE. For Detasheet D and Comp C, the reflected shock in the SS end plug was large enough to put the outer confinement tube in tension to cause failure. For these two more energetic explosives, their thickness was held constant 65% of the capsule length and then tapered to zero thickness at the end of the capsule. This modification reduced the amplitude of the transmitted shock so that hermetically sealed capsules could be routinely recovered.

To examine compression curves where the temperature increase is less than on the principal Hugoniot,

1D experiments could be performed where PE is sandwiched between two steel plates. An alternative approach we used was to make composite PE/Cu samples, because these composite samples could be easily employed in our present cylindrical capsules. Copper particles, 18- μ m-diam, were uniformly distributed in PE. A volume per cent of PE/Cu that could easily be processed was 57.3% PE/42.7% Cu. This composite sample and the sandwiched sample have similar dynamic behavior in that the final shock state is a result of a multi-shock process. This is the major factor in the reduction of temperature increase during shock loading. Of lesser importance is the heat conduction between the colder Cu particles and the hotter PE after the passage of the Mach wave. Similar conclusions on temperature increase can be reached using mixture EOS theory.

3. RESULTS

Recovery experiments on PE showed that the HP phase transition was related to the irreversible dissociation of the polymer chains into a dense molecular phase. To determine the molecular composition of the dissociation products a mass spectrometer (MS) was used. Initially, the dissociation products to be analyzed were contained in the recovery capsules at ~ 1.5 GPa (150,000-lb/in²) pressure. To transfer these gases from the recovery capsules to the MS, a special fixture was designed and built. Some gas was lost from most of the recovery capsules during the initial extraction procedure when the capsule was punctured. Therefore, for most of our experiments the absolute number of moles of gas in the recovery capsule could not be determined. However, the relative molar concentrations of the constituents were determined with excellent precision. A summary of the experimental results is presented in Table I. Using the EOS data of CM and the detonation velocities of the explosives, the Mach disk pressure under steady state 1D compression are respectively 13.3, 19.0, and 25.0 GPa. The relative molar concentrations of the dissociation products are listed for each experiment.

NM, Detasheet D, and Comp C were also used to shock compress the composite PE/Cu samples. For these experiments the diameter of the Mach disk was approximately 1/3 to 1/2 the sample diameter. Consequently, as will be explained later, a 1D compression of the sample occurred in the Mach disk. Using a mixture EOS⁴ for the composite PE/Cu samples (sample den-

y 4.34 gm/cm³), Mach disk pressures for the above explosives are respectively 68, 95, and 124 GPa. The relative molar concentrations for these experiments are so listed in Table I. It is evident that dissociation occurs at a much higher pressure for these multiple-shock states than for single-shock states. This is graphic illustration that temperature, not pressure (strain), is the dominant variable influencing dissociation.

Table I. Polyethylene dissociation products from cylindrical recovery experiments.

Sample	Explosive	P(GPa) 1D/CMD	Dissociation Products (mole %)				
			CH ₄	H ₂	C ₂ H ₆	C ₃ H ₈	Other
PE-1688	NM	13/18	No dissociation				
PE-1741	NM	13/18	No dissociation				
PE-1670	Detasheet D	19/27	86	9	4	0	1
PE-1738	Detasheet D	19/27	77	4	13	4	2
PE-1580	Detasheet D	12/27	76	4	13	4	3
PE-1662	Comp C	25/40	82	16	1	0	1
PE-1737	Comp C	25/40	81	5	10	3	1
PE-Cu-1735	NM	68/-	No dissociation				
PE-Cu-1762	Detasheet D	95/-	84	1	10	2	4
PE-Cu-1763	Comp C	124/-	70	3	13	3	11

The solid residue from the shock-loaded polyethylene was metallurgically examined to characterize its structure and morphology. The residue was characterized utilizing X ray diffractometry and Transmission Electron Microscopy (TEM). Bulk x ray analysis of the shock products revealed that the residue is a composite of several constituents, none of which correspond to the structure of the starting polyethylene material. X ray analysis conclusively ruled out the presence of either cubic or hexagonal diamond or hexagonal graphite. TEM examination of the polyethylene residue was conducted to determine the morphology of products and further examine the fine scale structure using selected area diffraction (SAD) techniques. The overall morphology of the shock residue was found to consist of several components. The bulk of the residue was found to be amorphous carbon "soot" particles, in the form of small ellipsoids most often in pairs. Both the size and chain like morphology are similar to previous studies on carbon soot, such as phylack. The ellipsoidal soot particles had dimensions between 0.3 and 0.8 μm . In addition to the soot particles, small chunks of a denser phase were often observed. The denser chunks had general overall dimensions of 0.3 to 3 μm . SAD analysis showed a crystalline

phase whose structure did not match any known diamond or graphite phase. The lattice spacings measured revealed a hexagonal structure with a = 8.95, b = 8.95, and c = 2.81 angstroms. These "a" and "b" spacings measured are consistent with the Claoite phase,⁵ however, the "c" lattice parameter is a curious multiple of five smaller.

DISCUSSION

The Mach compression waves in our cylindrical recovery systems are inherently stable after a few diameters of run. A typical assumption is that the Mach disk pressure can be calculated from the Hugoniot equations, since 1D flow is assumed. For cases where the Mach disk (MD) diameter is less than the sample diameter, as in our PE/Cu recovery experiments, this assumption is valid. Unfortunately, in the PE recovery experiments the MD diameter exceeded the sample diameter. When this occurs, a stable convergent Mach compression wave is formed. The sample pressure for these "over driven" Mach waves (MW) varies with sample diameter for a given explosive thickness. The variation of the MD pressure for our prototype Comp C recovery system is given in Fig. 2. In this example the sample was polymethylmethacrylate (PMMA) and a two dimensional (2D) Eulerian code was used to calculate the results. For MW diameter less than the sample diameter the pressure equals 36 GPa, the 1D Hugoniot pressure for this shock detonation velocity. With decreasing sample diameter, the MW diameter ultimately becomes larger than the sample diameter. When this occurs, the MW pressure monotonically increases with decreasing sample

diameter until the Hugoniot pressure (157 GPa) in SS was reached that corresponds to the shock velocity equal to the Comp C detonation velocity. This maximum pressure condition corresponds to zero sample diameter.

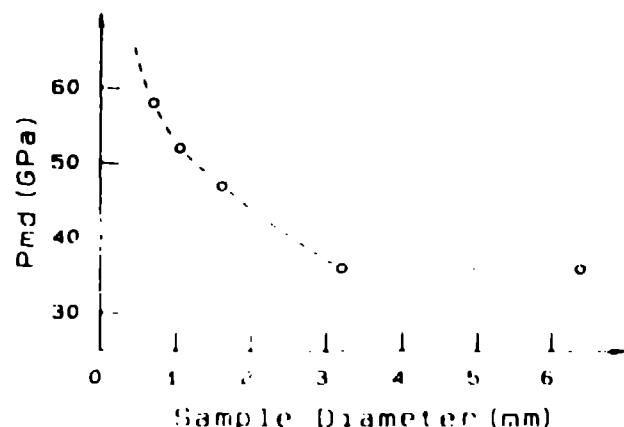


FIGURE 2
Mach disk pressure variation with PMMA sample diameter for a given capsule/explosive geometry.

It is important to emphasize the steady state MW velocities in all these calculations are equal to the detonation velocity of Comp C. The only difference is that for MW diameters greater than the sample diameter the Mach compression wave changes from a quasi 1D compression wave to a convergent compression wave. The calculated MW pressures in our PE recovery experiments are given in Table I. In all cases the convergent Mach disk (CMD) pressures are considerably greater than the 1D MW pressures. CM observed a high-pressure phase transition in PE at approximately 3 GPa. This is in agreement with our recovery results if the CMD pressures are used rather than the 1D Hugoniot pressures.

A theoretical EOS model was used to calculate the shock/release behavior of PE. The dissociation products were intentionally restricted to be carbon, H_2 , and CH_4 , because accurate potentials were available for these products. It was observed that small changes in molecular potentials altered the calculated dissociation products significantly. However, the trends discussed below still apply. On the PE Hugoniot the calculated temperature was 1,470 K at 25 GPa and increased to 2,700 K at 50 GPa. Over the same pressure range, the relative molar composition of H_2 , H_4 changed from 0.4%/99.6% to 1.9%/98.1%. Increasing temperature favors H_2 over CH_4 . Molar com-

positions were also calculated on release isentropes over this same Hugoniot pressure range. Only trivial changes in the molar concentration were observed upon release to the initial volume. In the absence of any strong reshocks, the composition of the products observed in the recovery capsules is indicative of the composition on the Hugoniot. However, our 2D Eulerian calculations showed reshocks of the order of 2 to 3 GPa. These reshocks could result in a significant temperature increase because the PV work could be significant. If this is the case, the H_2 concentration would be expected to increase due to the large temperature increase associated with these reshocks. In making comparisons between calculations and experimental results, an inherent uncertainty is present because one does not know when chemical reactions freeze out as the sample cools. In general, however, the observed dissociation products and theoretical calculations are in good qualitative agreement.

ACKNOWLEDGEMENTS

We would like to thank Walter Quintana for welding the recovery capsules and performing the recovery experiments, Bill Grant for designing and building the fixture used to extract the high-pressure gases from our recovery capsules, John O'Rourke for x-ray diffraction analysis of the recovered samples, and Stan Marsh for 2D Eulerian calculations used to interpret our experiments.

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